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PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The monthly meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 6th, the President (Dr. Stevenson) occupying the chair.

The minutes of the previous meeting were read and confirmed.

Mr. D. J. O'Mahony, F.C.S., Public Analyst for the city of Cork and for the county of Cork, was proposed for election as a member of the Society.

Mr. Hehner then read the following paper :

ON THE DETERMINATION OF THE BROMINE ABSORPTION OF FATS GRAVIMETRICALLY.

By Otto Hehner.

It is not the writer's intention to add another to the already numerous modifications of processes intended for ascertaining the haloid absorption of unsaturated fatty compounds. The Hübl process, evolved from the bromine absorption process first described by Allen (*Pharmaceutical Journal*, September 25, 1880), and which is substantially the same as that used by Mills and Snodgrass (*Soc. Chem. Ind.*, 1884, No. 64), and Mills and Akitt (*Soc. Chem. Ind.*, 1884), is however, after all, merely a conventional one, and only gives concordant results when worked under exactly comparative conditions, from which, as laid down by Hübl, it is not desirable to depart. The process certainly does not measure the iodine absorption of any oil, but probably the iodochloro-absorption. From iodine solution, without the addition of mercuric chloride, as used by Gantter (*Zeitsch. f. Anal. Chem.*, 1893, p. 81), Dieterich, and others, oils take a far smaller percentage of iodine than corresponds to the Hübl number; and the proportion of mercuric chloride used has an immense influence upon the result. The present contribution is, therefore, merely intended as a study, and not as a proposed method, although I believe that in some cases it may be found both convenient, and that it may afford another factor in judging of the constitution of an oil.

The instability of the Hübl solution is a great drawback to its use. When many determinations are made this is not a matter of much moment, but when only occasional determinations are to be carried out the solution must always be freshly prepared and standardized; this gives an amount of trouble out of proportion to the result aimed at, and has the further disadvantage that freshly made solutions are apt to give capricious results.

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In such cases a gravimetric method is always to be preferred to a volumetric one; the former has the additional advantage that the products of the reaction are obtained in such a form that their physical properties can be afterwards investigated, a matter, which, unfortunately, has been entirely neglected with the haloid addition products of oils, although promising valuable information.

If to an oil bromine is added, without the intervention of a solvent, combination takes place immediately; the reaction is, however, in many cases rather violent. By diluting with a suitable solvent, preferably chloroform or carbon tetrachloride, the action, though moderated, is equally complete.

A varying amount of hydrobromic acid is at the same time formed, and this is attributed by Mills to the presence of water in the materials; but is far more likely due to the formation of substitution compounds, besides the additive compounds. That this is so appears to me to be proved by some experiments which (following McIlhiney) I have made: Bromine added to chloroform containing some water produces no acid whatever, for when potassium iodide is added to such a mixture after a little time and in sufficient amount to convert the whole of the free bromine into a corresponding amount of iodine, and after the latter has been acted upon by an excess of hyposulphite solution, the resulting solution is perfectly neutral to phenolphthalein. This more or less roundabout method is necessary for testing, because iodine plus a hyposulphite yields tetrathionate and iodide without alteration of the reaction, while free bromine oxidizes the hyposulphite into sulphate, free sulphuric acid and free hydrobromic acid. The amount of free acid formed when bromine acts upon oil gives a measure for the amount of substitution. P. C. McIlhiney (*Jour. Am. Chem. Soc.*, 1894, p. 275; ANALYST, 1894, p. 141) has utilised in the manner previously employed and described by Allen (*Com. Org. Analysis*, ii., 383) the determination of the free acid formed as a measure of the substitution as distinguished from the addition. I have obtained the following figures: A sample of pure olive oil, treated with bromine, yielded 1·5 per cent. of free hydrobromic acid, another sample 2·7 per cent., castor oil 2·7 per cent., butter-fat 0·9 per cent., but a sample of boiled linseed oil 8·87 per cent. My figures, as far as they go, corroborate those found by McIlhiney, with the exception that he finds that no free acid is formed by the action of bromine upon boiled linseed oil. I know nothing about the origin of the sample tested by myself, and it is quite possible that it might contain either rosin or some other adulterant.

I operate as follows in order to obtain the bromo-compounds in a state fitted for weighing: A small, wide-mouthed fat flask is carefully weighed, and from 1 to 3 grammes of the fat to be tested introduced into it. These are dissolved in a few c.c. of chloroform, and then pure bromine is added, drop by drop, until the bromine is decidedly in excess. Both the chloroform and bromine must be previously tested in a blank experiment, to make sure that they contain no appreciable residue. The flask is then heated on the water-bath till most of the bromine is driven off; a little more chloroform is added, and the mixture again heated, the chloroform vapour helping to drive out the excess of bromine. The addition of chloroform may once more be repeated. The flask and its contents are then placed in an air-bath regulated for about 125° C., and kept there until their weight is constant; this takes

several hours. A little acrolein and hydrobromic acid escape during the drying, and the residue in some cases darkens slightly ; in others a clear yellow heavy bromo-oil is obtained. Drying at 100° C. does not lead to satisfactory results.

The following are some of the results, as compared with the Hübl figures, upon the same samples. For comparison, by multiplying with 1·587, I calculate the gain in weight of the oil into iodine :

Substance.	Iodine by Hübl.	Iodine corresponding to Bromine gravimetrically.
Olive oil	80·3 ...	81·5
,, ...	80·2 ...	79·9
,, ...	80·6 ...	80·7
Lard	65·7 ...	64·4
,, ...	,, ...	64·6
,, ...	63·2 ...	64·1
,, ...	60·1 ...	61·4
Maize oil	122·0 ...	123·2
Butter-fat	34·0 ...	34·3
Mutton-fatty acids ...	48·1 ...	47·8
Castor oil	83·0 ...	69·5
Boiled linseed oil ...	132·5 ...	159·5
Almond oil, fatty acids	— ...	102·3

In the case of the almond oil the Hübl figure was not determined, but calculating upon 95·5 per cent. of fatty acids in almond oil, the figure 102·3 for the fatty acids corresponds to 97·7, which is that given by the Hübl method for pure almond oil.

It will be seen that in most cases the iodine figure calculated from the gravimetric bromine absorption is in satisfactory approximation to the Hübl number, considering that that number is liable to variations of from 1 to 2 per cent., even in duplicate analyses (Amthor and Zink, *Zeitsch. Anal. Chem.*, 1892, p. 536). But in the case of castor oil the bromine process, as used by myself, gives a substantially lower result than the Hübl method ; while in that of the sample of boiled linseed oil the reverse is the case. Whatever the explanation of this may be, and without desiring to generalize upon such scanty data, it is remarkable that in both those cases, where the oils contained more oxygen than ordinary oils do, the figures are substantially different. This difference may be worthy of further investigation. W. Fahrion (*Chem. Zeit.*, 1892, xvi., p. 1472) has already shown that the behaviour of castor oil towards Hübl solution is anomalous.

The numbers obtained by Mills, in concert with his two collaborators, in a few corresponding cases (*loc. cit.*), may be usefully cited here. I have calculated Mills's bromine figures into their iodine equivalents (80 Br : 127 I) :

Substance.	Mills's Figure, as Iodine.	Average Hübl Number.
Almond oil ...	85·3 ...	96—99
Maize oil ...	118·1 ...	119
Olive oil	95·2 ...	82—85
,, ...	85·7 ...	,,
Castor oil ...	92·6 ...	83—84
Butter-fat ...	44·3 ...	26—38
Lard	59·2 ...	50—67
Linseed oil ...	120·7 ...	148—183
,, (boiled)	162·6 ...	—

Thus the Mills figures in almost every case agree very indifferently with the Hübl numbers. Curiously enough, Mills found a higher bromine number for castor oil than corresponds to the Hübl number; while for boiled linseed oil he finds actually a higher absorption than that of fresh linseed oil, when the contrary might be expected.

I would point out another curious fact, namely, that while unsaturated fats take up from an iodine solution, without the intervention of mercuric chloride, some iodine, showing that some iodo-addition compound is formed, it is not possible to obtain any gravimetric iodine addition number by acting upon such oils with iodine and drying the product. The iodine gradually volatilizes from the product, the weight of which decreases till it is not more, but sometimes even less, than that of the fat originally taken. The mass at first becomes green, then darkens much, almost chars at 125° C., and its melting-point rises considerably, solid fatty acids being formed. This is well known to be the case at very high temperatures, Wilde and Reichler (*Bull. Soc. Chem.*, 1889, No. 1, p. 295) having shown that oleic acid, heated with 1 per cent. of iodine to 270—280° C., yields about 70 per cent. of stearic acid. From my experiments it is obvious that this reaction takes place at much lower temperatures than these.

Discussion.

Mr. Allen said he thoroughly agreed with Mr. Hehner that the reaction occurring in the Hübl method of determining iodine absorptions was far from being understood. He thought the investigation of the products formed in the process would afford new and important information. Thus if, after the titration was finished, chemists would take the trouble to evaporate the chloroform and weigh the residue, the weight of the residue would show whether the product was a chloro-iodo-derivative or an iodo-derivative pure and simple; though he gathered from Mr. Hehner's paper that iodo-compounds prepared in other ways were so unstable as to decompose with facility. The plan employed by McIlhiney of ascertaining the amount of hydrobromic acid formed, and hence deducing the extent to which substitution had occurred, was a method devised by him (Mr. Allen), and found very useful in examining the action of bromine on hydrocarbon oils. He congratulated Mr. Hehner in having hit on so short and easy a method of working, and should await with interest the further development of the process. Although he (Mr. Allen) was the originator of the idea of determining bromine absorptions, or, at least, the first to use and publish a workable process, the employment of the bromine in solution in a menstruum free from water was due to Mills and Snodgrass, whose method of working possessed distinct advantages. It was a remarkable fact that in certain cases the bromine absorption could not be calculated to the corresponding iodine absorption by the factor $\frac{127}{80}$. In 1886, the speaker pointed out the anomaly in the case of the results recorded for almond oil in 1886 (*Journ. Soc. Chem. Ind.*, vol. v., p. 282), and believed in this case some error must have existed in Mills' determination of the bromine absorbed.* But

* Mills and Snodgrass found the bromine-absorption of the fatty oil expressed from bitter almonds (from which the commercial oil of almonds is chiefly obtained) to be 26·3, while the oil from sweet almonds absorbed 53·7 per cent. of bromine.—A. H. A.

another curious anomaly exists in the case of linseed oil, which when raw was found by Mills and Snodgrass to take up 76·0 per cent. of bromine (=120·7 per cent. of iodine), whereas boiled linseed oil absorbed 102·4 per cent. of bromine (=162·6 iodine absorption). It was remarkable that a somewhat similar result should have been obtained by Mr. Hehner.

Mr. Richmond said he had had some experience with the Hübl process as applied to butter, and his figures were higher than the usual average. He frequently started the experiment at night, and made the titration the next morning, following in this Archbutt's recommendation. Somewhat higher results were obtained in this way than by allowing two hours for the action of the solution on the oil, the increase sometimes amounting to 4 or 5 per cent. in oils of high iodine absorption. It was very desirable that the process should be so arranged as to avoid such discrepancies if possible. If Mr. Hehner's process gave constant results—as it seemed to promise—it would be in many ways superior to the iodine absorption process.

The President said the paper was an extremely interesting one, especially in the close agreement of the figures, and the facility with which gravimetrical measurements of the bromine compounds could be made. He hoped Mr. Hehner would be able to continue his investigations, and emphasized what Mr. Allen had said with regard to the desirability of examining the residues. He thought that the Hübl process might be satisfactorily worked by substituting a compound of iodine and chlorine for mercuric chloride.

Mr. Hehner, in reply, said it was regrettable that the haloid absorption processes had been worked volumetrically in every case; it seemed desirable to him that the products of the reaction should be studied as to their physical and other characters. The nature of the reaction involved in the Hübl process was far from clear; only very few, if any, figures obtained by the action of Hübl solution on pure unsaturated fatty acids had been published—indeed, it seemed exceedingly improbable that any pure unsaturated olein acid had ever been prepared. When the formula of oleic acid was established nothing whatever was known of linoleic and linolenic acids, and the earlier investigators had, indeed, obtained their so-called oleic acid from linseed oil, which was now known to contain hardly any oleic acid at all. The explanation generally accepted as to the action of Hübl reagent was that the free iodine dislodged an equivalent amount of chlorine from the mercuric chloride, mercuric iodide and iodine chloride being formed; but if this were correct, there ought to be a separation of mercuric iodide, and this, as far as he knew, had never been observed. He thought the suggestion of the President as to dispensing with the use of mercury a valuable one, and he would try the use of a solution of iodine chloride instead of the Hübl solution. Mr. Richmond's remarks illustrated what he had said at the beginning of his paper, namely, that the tendency was for every chemist to make his own modification of the Hübl process, and as a consequence different workers often obtained widely divergent results, and this was hardly fair to the Hübl process itself.

Mr. Richmond then read the following three papers :

THE COMPOSITION AND ANALYSIS OF MILK AND MILK-PRODUCTS.

By H. Droop Richmond.

This paper is a continuation of the annual reports of the work done in the laboratory of the Aylesbury Dairy Company. The results obtained in 1894 are given in the present communication. (For previous reports, see Analyst, vii., 53; viii., 33; ix., 56; x., 67; xi., 66; xii., 39; xiii., 46; xiv., 69; xv., 44; xvi., 61; xvii., 62; xviii., 50; and xix., 73.)

The total number of samples analysed in 1894 was 32,295, consisting of

28,455	samples of	milk.	2,269	samples of	cream.
706	,,	separated and skimmed milk.			
174	,,	butter.	18	,,	buttermilk.
22	,,	water.	38	,,	sundries.
613	,,	bacteriological examinations.			

Of the milk-samples, 12,633 were, in order to check the quality of the milk received, taken from the railway churns on their arrival at the company's chief depot. The bulk of the milk is distributed, with the least possible delay, to the customers, a certain portion being, however, utilized for the production of cream, etc. To control the men employed in delivering the milk, a further 13,361 samples were taken before, during, and after delivery, and analysed comparatively.

The fat has been estimated this year by the Leffmann-Beam method, and the total solids were calculated by the milk-scale.

Average Composition of Milk during 1894.

	On Arrival.				Before Delivery.	During Delivery.	After Delivery.
Month.	Sp. Gr.	T. S.	Fat.	S.-n.-F.	T. S.	T. S.	T. S.
January ...	1·0322	12·84	3·98	8·86	12·74	12·80	12·75
February ...	1·0322	12·66	3·82	8·84	12·61	12·60	12·57
March	1·0322	12·57	3·74	8·83	12·55	12·50	12·53
April	1·0320	12·52	3·75	8·77	12·51	12·46	12·46
May	1·0323	12·47	3·66	8·81	12·44	12·41	12·37
June	1·0323	12·48	3·68	8·80	12·47	12·45	12·42
July	1·0319	12·44	3·74	8·70	12·43	12·38	12·36
August ...	1·0320	12·50	3·75	8·75	12·40	12·38	12·37
September ...	1·0322	12·62	3·81	8·81	12·57	12·51	12·52
October ...	1·0321	12·74	3·93	8·81	12·63	12·63	12·66
November ...	1·0322	13·14	4·24	8·90	12·95	12·97	13·04
December ...	1·0323	13·07	4·18	8·89	12·83	12·91	12·82
Average ...	1·0322	12·67	3·86	8·81	12·60	12·59	12·57

The figures differ but very slightly from those of last year. As is usual, the poorest milk is found in the summer, and the maximum is attained in November.

In comparing the different columns, it must be remembered that not only are

the samples taken at random, and are not directly comparable, but that, for the control of the business, more attention is naturally paid to milk the quality of which is known or suspected to be below the mean (*e.g.*, the morning's milk, which is always poorer than the evening's), than to that which is above the average. Allowing for this, the agreement of the averages is almost absolute.

Cream samples were taken before and during delivery. The average of the results is given in the following table:

AVERAGE AMOUNT OF FAT IN CREAM DURING 1894.

Month.	Before Delivery.	After Delivery.
January	46·7	46·5
February	47·9	47·9
March	49·1	49·4
April	48·6	48·8
May	49·4	49·6
June	48·7	48·4
July	48·5	49·6
August	51·0	51·2
September	48·4	49·2
October	47·6	48·3
November	48·6	48·6
December	50·8	50·5
Average	48·9	49·1

Considering the difficulty of drawing average samples of cream of such richness the agreement between the two series is satisfactory.

The Leffmann-Beam method is now adopted also for cream analysis, with very satisfactory results.

The average composition of 44 samples of clotted cream is as follows:

AVERAGE COMPOSITION OF CLOTTED CREAM DURING 1894.

Water	31·59
Fat	60·25
Ash	·69
Solids-not-Fat	8·16

These figures are not greatly different from those found in former years.

The amount of fat in separated milk was in most cases less than 0·3 per cent., and on very rare occasions was it found to be above 0·4 per cent.

The composition of the butter analysed was as follows:

AVERAGE COMPOSITION OF BUTTER DURING 1894.

French Butter, fresh; 41 samples.

Water	14·32 to 12·78	average	13·60
Fat	86·09 ,, 84·19	,,	85·05
Solids-not-Fat	2·47 ,, ·78	,,	1·35
Salt	·19 ,, ·03	,,	·09
Ratio of water to solids-not-fat, less salt		,,	9·2

French Butter, salt; 31 samples.

Water	13·57 to 9·68	average	11·27
Fat	87·72 ,, 82·98	,,	85·28
Solids-not-Fat	4·63 ,, 1·96	,,	3·45
Salt	3·29 ,, ·57	,,	1·97
Ratio of water to solids-not-fat, less salt ...		,,	13·1

Brittany Butter; six samples.

Water	14·81 to 13·75	average	14·26
Fat	84·36 ,, 83·18	,,	83·84
Solids-not-Fat	2·01 ,, 1·78	,,	1·90
Salt	·25 ,, ·09	,,	·16
Ratio of water to solids-not-fat, less salt ...		,,	12·2

English Butter, fresh; 22 samples.

Water	15·23 to 11·90	average	13·49
Fat	87·62 ,, 84·03	,,	85·70
Solids-not-Fat	1·83 ,, ·48	,,	·81
Salt	1·07 ,, ·01	,,	·14
Ratio of water to solids-not-fat, less salt ...		,,	5·0

English Butter, salt; 46 samples.

Water	16·39 to 10·19	average	13·11
Fat	87·65 ,, 79·99	,,	83·94
Solids-not-Fat	5·16 ,, 1·90	,,	2·95
Salt	4·30 ,, ·90	,,	2·11
Ratio of water to solids-not-fat, less salt ...		,,	6·4

Australian and *New Zealand* Butters, salt; 6 samples:

Water	12·53 to 8·24	average	10·72
Fat	89·82 ,, 85·41	,,	87·21
Solids-not-Fat	2·59 ,, 1·44	,,	2·07
Salt	1·55 ,, ·92	,,	1·23
Ratio of water to solids-not-fat, less salt ...		,,	7·9

An opportunity occurred for studying the change in composition in butter kept in casks. A salt butter was kept in a cask for one month, and was analysed directly after churning, and after one month:

	Water.	Fat.	S.-n.-F.	Salt.	Ratio of water to S.-n.-F. less salt.
Fresh	15·24	79·99	4·77	3·96	5·3
One month old ...	11·08	85·73	3·19	2·61	5·2

The diminution in solids-not-fat and salt show that the water had run out, and was not lost by evaporation. The salt has diminished in rather greater ratio than the water. This fact I have observed in butters kept in paper wrappers, and is possibly due to osmosis.

The results of the analysis of the fat are given in the following table:

ANALYTICAL RESULTS OF BUTTER FAT DURING 1894.

	French Butter.	English Butter.	New Zealand and Australian Butter.
Reichert-Wollny ...	33·2 to 28·2 av. 30·6	32·3 to 24·1 av. 28·1	31·0 to 27·5 av. 29·1
Potash absorbed ...	22·88 ,, 22·49 ,, 22·65	22·83 ,, 22·01 ,, 22·56	
Iodine ,, ...	40·2 ,, 31·3 ,, 37·0	38·9 ,, 37·1 ,, 37·9	Brittany Butter.
Density $\frac{39{\cdot}5^\circ}{39{\cdot}5^\circ}$ ...	·91165 ,, ·91123 ,, ·91143	·91174 ,, ·91036 ,, ·91116	R.W. 28·8 to 28·6 av. 28·7
,, $\frac{39{\cdot}5^\circ}{4^\circ}$ ...	·90484 ,, ·90442 ,, ·90462	·90493 ,, ·90356 ,, ·90436	
,, $\frac{100^\circ}{15^\circ}$ ...		·8654 ,, ·8652 ,, ·8653	

THE RELATION BETWEEN SPECIFIC GRAVITY, FAT, AND SOLIDS-NOT-FAT IN MILK.

By H. Droop Richmond.

In the Analyst (xix., 65) I proposed a new formula, $T = \cdot 2625 \frac{G}{D} + 1 \cdot 2\ F$, for calculating fat from total solids and specific gravity, and *vice-versâ*. It was calculated from a considerable number of analyses made as accurately as possible, and using methods which seemed to me to be those most free from error.

Further series of analyses have shown that the results by this formula agree very much better with the actual results than those obtained by the milk scale. Evidence is not wanting that others have found that the fat calculated by the milk scale is slightly higher than that estimated. Thus Embrey (Analyst, xviii., 120) states that he finds an average difference of 0·1 per cent., and proposes, and has even published, a set of tables corrected by this difference. More than one analyst has verbally informed me that in his laboratory the same thing has been noticed. In the "Proceedings of the Tenth Annual Convention of the Association of Official Agricultural Chemists," p. 108, a series of results was obtained showing that this new formula agrees better than any other, though, as it was not before them, it was not actually considered.

For these reasons I have calculated a table, by reference to which the total solids can be calculated from the specific gravity and the fat. This form of table is, I believe, the most useful now that rapid processes of fat-estimation are generally used, and the data used in a preliminary examination of milk are fat and specific gravity.

As the table is necessarily somewhat large, and it is frequently more convenient to calculate the results directly than to look them up in a table, I have endeavoured to simplify the formula without greatly detracting from the accuracy.

The formula $T = \cdot 2625 \frac{G}{D} + 1 \cdot 2\ F$ may be written:

$$T = \cdot 2625 \left(\frac{G}{\frac{1000 + G}{1000}} \right) + 1 \cdot 2\ F,$$

and, expanding this in terms of G, we get:

$$T = \cdot 2625\ (G - \cdot 001\ G^2 + \cdot 000001\ G^3 \ldots) + 1 \cdot 2\ F.$$

The first three terms only need be taken into account. This is equal to

$$T = \cdot 25\ G + (\cdot 0125\ G - \cdot 0002625\ G^2 + \cdot 0000002625\ G^3) + 1 \cdot 2\ F.$$

Now, for values of G likely to be obtained in practice—*i.e.*, 20 to 36—the expression $\cdot 0125\ G - \cdot 0002625\ G^2 + \cdot 0000002625\ G^3$ is nearly constant, and is equal to $0 \cdot 14 \pm 0 \cdot 02$.

Therefore the formula may be written:

$$T = \frac{G}{4} + \frac{6}{5}\ F + \cdot 14,$$

and the results will not differ (in extreme cases) more than ·02 from the other formula.

We find also that, if the fat is 3 per cent., the value of 0·05 F is 0·15, and is nearly equal to ·0125 G – ·0002625 G^2 + ·0000002625 G^3, and the formula may be written:

$$T = \cdot 25\ G + 1 \cdot 25\ F, \text{ or } T = \frac{G + 5\ F}{4},$$

and this second simple formula is correct within 0·2 per cent. up to 6 per cent. fat. It is still more accurate if 0·05 per cent. be added for each 1 per cent. above 3 per cent., and subtracted for each 1 per cent. below 3 per cent.

A milk scale to express the same relation may be constructed on which 1 per cent. total solids = 1 inch, 1 per cent. fat = 1·2 inches, or 5 per cent. = 6 inches, and 1 degree of gravity = $\frac{1}{4}$ inch; if the zero on the fat scale be placed on a line with 5 per cent. on the total solid scale, the arrow will be in its correct position, 0·14 ($\frac{1}{7}$) inch below 20 degrees on the specific gravity scale.

It will be remembered that Hehner and I gave as a simple formula $T = \frac{G}{4} + \frac{6}{5} F$; Babcock (*Ann. Report Wisconsin Exper. Stat.*, 1891, p. 298) has given the formula $T = \frac{G + 5\ F}{4}$ in a slightly different form.

By placing an arrow 0·14 ($= \frac{1}{7}$) inch below the present arrow, existing milk scales will give a near approximation.

MAUMENÉ'S TEST FOR OILS.

By H. Droop Richmond.

After an extended trial of the various methods and forms of apparatus for performing the Maumené test which have been proposed from time to time, and after a study of the various reactions, so far as can be ascertained, which take place in that process, I have been led to devise the following method of procedure. By means of this modification, I feel assured that results more uniform and exact than those hitherto attainable can be secured:

Calorimeter.—A small, deep beaker is fitted inside a slightly larger one by means of a ring of cork; the outer beaker is placed in a tin cup padded with cotton-wool. The heat-capacity of this is estimated by placing 10 grammes of water inside, noting the temperature, and pouring in about 25 grammes of warm water (of known temperature), and noting the resulting temperature. The cooling in this calorimeter during a Maumené test does not amount to more than 1 per cent., and may be neglected.

Influence of Strength of Acid.—Between the limits, 92 per cent. to 100 per cent. H_2SO_4, the rise of temperature is directly proportional to the strength of acid (difference not more than 1 per cent.).

Heat-Capacity of Mixture of Oil and Acid.—25 grammes of oil and 5 c.c. of sulphuric acid, when mixed, have a heat-capacity about equal to that of 20 grammes of water.

The total heat evolved per mean molecule may be calculated; this I call the "Relative Molecular Maumené" figure:

Let x = percentage of H_2SO_4 in acid (100 per cent. H_2SO_4 assumed as standard strength);
h = heat-capacity of calorimeter in grammes of water;
R = observed rise (25 grammes oil, 5 c.c. acid);
K = potash absorbed (19·5 per cent. KOH is assumed as a standard of comparison);

$$\text{then R.M.M.} = R \times \frac{21{\cdot}5}{x - 78{\cdot}5} \times \frac{20 + h}{20} \times \frac{19{\cdot}5}{K}.$$

This action of the acid on the oil is probably in two stages—(i.) hydrolysis, (ii.) action on the unsaturated bonds.

I believe that a definite amount of the heat evolved is due to hydrolysis, and the remainder to the second stage. My experiments indicate that the R.M.M. of hydrolysis lies between 7° and 18°, and is probably about 12°, and that glycerides containing acid radicles with two unsaturated bonds evolve more than twice the amount of heat than those with one unsaturated bond.

Contribution to Butter Analysis—The Abbé-Zeiss Refractometer. J. Delaite. (*Bull. de l'Assoc. belge des Chimistes*, 1894, No. 5, pp. 145-152.)—According to Zeiss, the refractive index may be taken at any temperature, and the reading subsequently calculated to a standard temperature, *e.g.*, 25°. But the author proves that this does not give concordant results with fats. Thus, the indices obtained from one butter, from readings taken at different temperatures and reduced to 25° C., were:

Temp. of Observation.	Refractive Index, calculated to 25° C.
45°	48·8
40°	49·3
35°	49·5
30°	49·65
25°	49·7

This inverse ratio of the refractive index to the temperature only occurs markedly in the case of pure normal butters. Abnormal and adulterated butters and margarines, though not giving constant results, show no order in their variation. Two margarines, for instance, gave the following results:

	Temperatures.					Indices calculated to 25° C.				
	45°	40°	35°	30°	25°	45°	40°	35°	30°	25°
Ref. Indices (1)	—	49·6	52·2	55·3	—	—	58	57·8	58·1	—
,, (2)	47	49·5	52·2	55	59·2	58·2	57·9	57·8	57·8	59·2

It is necessary, therefore, to select a definite temperature for taking the reading, and it is suggested that this should be 40° C. for fats and 25° for oils. By means of a current of warm water the temperature is brought to 45° or 50°, and is then allowed to fall very slowly to 40°. The error of reading introduced by the temperature of the whole instrument not being the same as that of the water, is thus avoided.

As to the value of the process, the author's opinion is that it cannot be relied upon to give alone even a preliminary decision as to the genuineness or otherwise of a butter. For although the average butter does not give a refractive index higher

than 44 at 40°, yet samples undoubtedly genuine often give higher figures. On the other hand, abnormal and adulterated butters have been known to give figures as low as 41·6 and 42. Moreover, rancidity appears to affect the result. A butter known to be adulterated was left for more than a year, and, when strongly rancid, gave a refractive index of 48·25 at 30°, while that of an average pure butter at that temperature is 52·5. Hence, judged by the refractive index alone, this sample would have been declared genuine. The addition of cocoanut oil or palm oil to a butter also lowers the index. The refractive index of the former varies from 33·2 to 35·2 at 40°, that of the latter from 35·2 to 45·3. A mixture of a pure butter with refractive index of 44 at 40°, with 20 per cent. of cocoanut oil, showed an index of 42·2. A similar result was also obtained by adding horse-fat to butter. C. A. M.

An Examination of the Twitchell Method for the Determination of Rosin in Soap. T. Evans and I. E. Black. (*Amer. Chem. Journ.*, 1895, xvii., I., pp. 59-67.)—Twitchell's process,* although the most satisfactory known, has been proved to be far from exact, especially when the gravimetric method is employed, in which, as has been shown by Lewkowitch, a loss of from 10 to 15 per cent. is frequent.† With the object of rendering it more accurate, the authors have made experiments on the same lines as Twitchell, preparing test-samples containing known quantities of rosin and fatty acids.

In the volumetric method, too high results were obtained when the combining weight of the rosin was taken as 346, the number given by Twitchell. At first this was attributed to incomplete etherification, but repeated titration proved that the combining weight of the sample was 328·9—a figure lower than any of those recorded by Twitchell or Lewkowitch. Taking this number as the factor, the results were much more accurate, as is shown in the following instances selected from a long table :

Percentage of Rosin.

Theory.	Combining Weight 346. Found.	Difference.	Combining Weight 328·9. Found.	Difference.
40·13	42·19	+2·06	40·10	−0·03
40·13	41·74	+1·61	39·67	−0·46
40·13	42·16	+2·03	40·06	−0·07

By leaving the alcohol saturated with HCl, and before diluting with water, all night on the water-bath, the results could be considerably lowered, and still more so by adding H_2SO_4 before this treatment. The substitution of methyl alcohol for ethyl alcohol gave poorer results, and if left all night before evaporating the alcohol caused considerable loss. The results were also too low if the water surrounding the flask during etherification became too warm, or if the current of HCl were too rapid.

By using ethyl alcohol, and boiling out soon after etherization, concordant results were obtained, approximating closely to the theoretical.

Attempts were made to etherize rosin alone, but in each case the results were too low.

* See Analyst, xvi., p. 169. † *Journ. Soc. Chem. Ind.*, xx., 1893.

Weight of Rosin.	Rosin calculated from Titration.	Difference.	Percentage loss.
2·0968 grms.	2·054	0·0428	2·00
2·4723 ,,	2·45	0·0223	0·90
2·035 ,,	2·016	0·019	0·93
2·03 ,,	2·016	0·014	0·69
2·115 ,,	2·091	0·024	1·14

With methyl alcohol the loss was still greater, being 6 or 7 per cent., a result probably due to decomposition.

As is shown in the first table, when the combining weight of a rosin is known the volumetric method is sufficiently accurate, but the combining weight varies greatly in different grades of rosins, ranging from 328·9 to 355·9. Accordingly, the authors made the attempt to separate the rosin in a given sample, determine its combining weight, and to use this number as the factor in the volumetric determination. A sample of resin (combining weight 328·9) was subjected to the gravimetric process, and the rosin acids dried at 105°, and titrated. The combining weights obtained were (1) 328·6, (2) 325·9.

Four similar experiments with a rosin with combining weight 351·4 gave the combining weights, 329, 323·9, 331·1, 329·4.

The explanation of these discrepancies was looked for in the loss which occurs in the gravimetric method. This loss was found to be in the petroleum ether layer from which the saponifiable rosin had been removed by caustic potash. A sample of rosin (combining weight 351·4) was treated as in the gravimetric method, and the residual petroleum ether, after removal of the rosin, evaporated to dryness, when a gum-like mass with a turpentine smell was left, corresponding to 9·71 per cent. of the original rosin. This residue was not saponifiable with alcoholic potash, and was therefore not an ether.

A mixture of fatty acids and rosin gave a loss of 5 per cent., which corresponded exactly with the percentage of unsaponifiable matter in the sample of rosin used.

Four other samples of rosin tested for unsaponifiable matter gave the following results:

Grade.	Unsapon. Matter per Cent.	Comb. Weight Original Rosin.	Calculated Combining Weight Saponifiable Rosin.
WW	7·34	339·9	315·0
WG	5·00	328·9	312·4
N	9·00	351·4	319·7
N	8·21	347·5	319·0
M	7·61	339·8	314·0
		Mean	316·0

The authors are investigating the subject further, and perfecting a method for the separation of the unsaponifiable rosin from the hydrocarbon oils used as soap-fillers, etc. C. A. M.

The Determination of Sulphur in Volatile Organic Compounds. C. F. Maybury. (*Amer. Chem. Journ.*, 1894, xvi. 544; through *Chem. Zeit.*)—The author has made a critical examination of various methods of determining sulphur, especially

in petroleum products, and has in particular examined the method of Carius and the process consisting in oxidizing the material to be analysed in a combustion tube in a stream of air or oxygen. The tube, which must be of refractory glass, is somewhat contracted in the middle; the stream of air or oxygen is let in through a piece of narrow tubing passing up to the point of contraction. The stopper which carries this narrow tube has a second perforation carrying a tube conveying carbonic acid, in order to drive the material to be analysed towards the forward end of the combustion tube. The products of combustion pass into a large U-tube containing 50 c.c. of caustic potash, of which each c.c. is equivalent to 1—5 milligrammes of sulphur, according to the content of the substance to be analysed. The liquid can be titrated in the U-tube itself, methyl orange being used as an indicator. B. B.

The Determination of Free Sulphuric Acid in Leather. P. F. Jean. (*Rev. Chim. Analyt.*, 1895, iii. 13; through *Chem. Zeit.*)—The process preferred by the author consists in extracting the dried and powdered leather in a Soxhlet apparatus with absolute alcohol containing a little caustic potash to fix the sulphuric acid. After thorough extraction, the alcohol is distilled off and the sulphuric acid determined in the residue as barium sulphate in the usual manner. B. B.

Thioacetic Acid as a Substitute for Sulphuretted Hydrogen in Analysis. R. Schiff and N. Tarugi. (*Gazz. Chim. ital.*, 1894, xxiv., vol. ii., 551; through *Chem. Zeit.*)—When a hydrochloric acid solution of the metals of the second group is treated with a slightly ammoniacal solution of ammonium thioacetate (30 per cent. strength) in the proportion of 1·5—2 c.c. for 1 gramme of the metals to be separated, and the mixture is warmed to 80-90° C., all the metals are precipitated as sulphides, although only a slight smell of sulphuretted hydrogen is perceptible. After cooling and filtering, the solution is found to be free from metals of the second group, and the analysis is completed in the ordinary manner.

Ammonium thioacetate is decomposed in the presence of hydrochloric acid with the formation of ammonium chloride, acetic acid, and sulphuretted hydrogen. Tin, bismuth, copper, platinum, and gold are only partly precipitated in the cold, but completely on keeping. Lead and mercury are precipitated in the cold as red chlor-sulphides, which on heating are converted into the ordinary black sulphides. With arseniates the reagent gives a slight white turbidity in the cold, but on heating the solution sudden and complete precipitation takes place. Cadmium sulphide dissolves in the warm hydrochloric acid, but again separates on cooling. Thioacetic acid reduces ferric salts and chromates.

The reagent is prepared by adding 10 per cent. ammonia solution in slight excess to thioacetic acid, and then diluting the mixture to treble the volume of the thioacetic acid used. The resulting liquid is yellow, and smells slightly of ammonium sulphide; it becomes turbid on heating, and needs to be freshly prepared every eight or ten days. The advantages which its use presents consist in avoidance of the smell of sulphuretted hydrogen, and of the need for a Kipp or similar apparatus; the rapidity and completeness of precipitation are also reasons for preferring this reagent. B. B.

The Phospho-molybdic Acid Test as applied to Lard Analysis. George F. Tennille. (*Jour. Amer. Chem. Soc.*, 1895, xvii. 1, pp. 33-41.)—The conclusion arrived at by Samelson (ANALYST, xix., p. 251), that the phospho-molybdate test is of little analytical value, is here confirmed. It will certainly detect the addition of a large quantity of cotton-seed-oil; but if only a slight green coloration be obtained, adulteration cannot be considered as proved.

The author's experiments were made with the three grades of lard constituting the bulk of that sold to the New York refiners—viz.:

No. 1 Lard.—Steam-rendered, and consisting of gut fat, with occasionally a little trimmings, but no leaf.

Prime City Lard.—Rendered either by steam or in open kettles, and consisting of trimmings, head, foot, and back fat, and sometimes a little leaf.

Prime Western Lard.—Steam-rendered; from gut fat, with occasionally trimmings.

All the samples of No. 1 lard examined gave the green coloration, and this was also the case with a sample rendered in the laboratory from No. 1 stock. This was No. 10 in the table.

Nearly all the City lards gave negative results. Of fifty-seven undoubtedly pure samples, fifty gave no coloration, and seven gave a slight green tinge.

The Western steam lard often gave a slight green colour, which, however, was not so pronounced as that obtained with No. 1 lard.

The following table gives the particulars of the tests applied to ten samples of No. 1 lard:

Hübl Figure.	Dalican's Titre °C.	Rise of Temperature with H_2SO_4 °C.	Becchi's Silver Test.	Milliau's Silver Test.	Phospho-Molybdic Acid Test.	Crystals from Ether Powder. Microscope.	Free Fatty Acid, per Cent.	Spec. Grav. 98°C:15°C.
1. 54·5	41·4	30·5	Negative.	Slight discoloration.	Decided green. Blue if alkaline.	Lard only.		
2. 55·6	41·4	31·8	,,	,,	,,	,,		
3. 58·6	40·2	34·8	,,	,,	,,	,,	0·73	0·8595
4. 53·7	41·4	30·0	,,	,,	,,	,,		
5. 55·4	41·4	31·5	Slight discoloration.	,,	,,	,,		
6. 56·1	41·4	31·7	Negative.	,,	,,	,,		
7. 47·7	42·4	25·5	Slight discoloration.	,,	,,	,,		
8. 51·7	41·8	31·5	Negative.	,,	,,	Indication of beef.		
9. 52·0	41·9	29·5	Slight discoloration.	,,	,,	,,		
10. 48·9	—	—	—	,,	,,	—		

As leaf lard does not give a green colour with the reagent, the author thinks that the favourable reception given to the test on its first appearance was due to the experimenters using that lard. C. A. M.

The Asphalt Question. S. F. Peckham. (*Jour. Amer. Chem. Soc.*, 1895, xvii., No. 1., pp. 55-63.)—In a critical review of various papers that have been pub-

lished on the chemistry and analysis of asphalt, the author states his objection to the method employed by Richardson of determining the amount soluble in CS_2, since that liquid does not dissolve all the bitumen. With Miss Linton's process,* in which the use of CS_2 is altogether discarded, he obtained very concordant results, agreeing to the third place of decimals. The petroleum ether used should be obtained from petroleum consisting of hydro-carbons of the paraffin series, and have a specific gravity of 0·7. D. Torrey's method, based on successive solutions of the asphalt in alcohol, does not offer any advantages over that proposed by Miss Linton.

C. A. M.

Rapid Estimation of Starch. P. L. Hibbard. (*Jour. Amer. Chem. Soc.*, 1895, xvii. 1, pp. 64-68.)—Of the methods for determining starch in crude celluloses, none can claim absolute exactness. Lintner's process of heating in closed vessels, under high pressure, with water or a weak acid, gives good results when soluble convertible carbo-hydrates other than starch are absent; while Märker's process, which is the most satisfactory, has the same drawback, more or less of the various gums present being dissolved by the diastase. In the latter process the substance is boiled for a few minutes with water to gelatinize the starch, and after cooling to 60° diastase is added, and the liquid maintained at 65° for an hour. The solution is then filtered, the filtrate treated with HCl, and the converted dextrose estimated by Fehling's solution (see ANALYST, xx., pp. 17-19).

A shorter and easier modification of this method is suggested by the author, the advantages of which over older processes are: (1) Prevention of clots by the addition of malt extract previous to heating; (2) prevention of lactic fermentation by rapid heating; (3) a minimum solution of bodies other than starch, owing to the short time of boiling.

The malt extract which is used instead of pure diastase is prepared by infusing the malt for several hours, with water containing 15 to 20 per cent. of alcohol, and filtering. The alcohol acts as a preservative, without interfering to any great extent with the diastatic power of the malt. The solution thus prepared will keep for a fortnight, even in warm weather.

In the estimation the finely-powdered substance is heated to boiling in a flask, together with 50 c.c. of water and one to two c.c. of malt infusion. (If the substance contain much fibrous material and but little starch, nothing is gained by adding the malt here, as the diastase is destroyed by the high temperature before it can act on the starch.) After boiling for a few minutes, the mixture is cooled to 50° or 60° C., and another two or three c.c. of malt extract added. It is then slowly heated for ten to fifteen minutes till boiling, again partially cooled, and tested with iodine solution. If any blue colour appear, the treatment with malt must be repeated. When all the starch is changed the liquid is cooled, made up to definite volume, and filtered through muslin or linen. An aliquot part, sufficient to contain 0·2 to 0·3 grammes of starch, is taken from the filtrate, and is boiled on a sand-bath, in a 100 c.c. flask, with 5 c.c. of HCl (30 per cent. gas), and sufficient water to make up about 60 c.c. No reflux

* ANALYST, xx., p. 41.

condenser need be used, and the conversion is complete after thirty minutes' actual boiling. When cool, the solution is neutralized with NaOH, and the dextrose estimated with Fehling's solution. Less than two hours is required for the determination. The following figures compare the results obtained by this method with those by the direct inversion method:

Material.	Moisture.	Starch per Cent.	
		Malt Method.	Acid direct.
Starch factory feed	10·0	10·0	40·9
Impure moist starch	12·0	81·3	82·3
,, ,, ,, ...	—	79·5	80·9
Good starch	12·8	84·3	84·6
Purified dried starch	—	95·1	96·5
Corn, large white kernels ...	11·0	63·5	68·2
Wheat, hard red variety ...	10·0	60·5	65·0
Bran from same wheat ...	11·3	28·4	44·4
Middlings from same wheat ...	10·1	53·8	60·0
Low flour ,, ,, ,, ...	10·2	66·0	67·7
Good flour ,, ,, ,, ...	11·0	67·9	69·0
Wheat flour	10·0	70·7	73·6
Wheat bran	10·1	29·3	46·5

C. A. M.

A New Method of Estimating Carbon in Iron. Leop. Schneider. (*Stahl und Eisen*, 1894, 1029; through *Chem. Cent. Blatt.*)—The author has found that the addition of powdered copper and lead to the iron causes the latter to burn much more readily in a current of oxygen. The lead is prepared by shaking the molten metal, and the copper by reduction of oxidized copper-wire in a current of hydrogen. In the estimation 3 grammes of the finely-divided steel are incorporated with 10 grammes of a mixture of three parts of lead-powder with one part of copper-powder, and introduced into the combustion-tube in a porcelain boat, below which is placed a little asbestos. In front of the boat is placed 10 to 20 cm. of copper oxide. After the boat has been brought to a dull red heat, the current of oxygen is admitted, and the metallic mixture readily takes fire. The gases produced, after being dried by H_2SO_4, are led into soda. After the combustion the current of oxygen is continued for another ten minutes. The whole operation requires three-quarters of an hour.

C. A. M.

On the Use of Litmus and Methyl Orange as Indicators in Volumetric Analysis. G. Lunge. (*Zeit. für angewandte Chemie*, 1894, 24, pp. 733-738.)—The author admits that litmus, when prepared and used according to Reinitzer's directions (ANALYST, xix. 255), is more sensitive than methyl orange, but denies that the superiority is as great as claimed. With 250 c.c. of distilled water, and using $\frac{1}{5}$ normal or decinormal acid, it is not eight times, but only twice, as sensitive. Since Reinitzer only gave comparative results when the indicators were used with distilled water, the author has made experiments to determine their merits when used with 50 c.c. of a $\frac{1}{5}$ normal soda solution. With normal acid practically identical results are obtained, but methyl orange is preferable on account of its speed and the

precautions to be observed in the use of litmus. With semi-normal acid the change of colour is more difficult to observe in the case of methyl orange, but a practised observer can be sure to a drop; and when liquids containing carbonic acid have to be frequently titrated, the gain of time is a compensating advantage. It is only with decinormal acid that litmus is undoubtedly superior, and Reinitzer's method of titration must be observed. C. A. M.

The Determination of Potash in Manures. W. E. Garrigues. (*Jour. Amer. Chem. Soc.*, 1895, xvii., No. 1, pp. 47-51.)—The process recommended depends on (1) conversion of all the potash present and removal of ammonia and organic matter by ignition with H_2SO_4; (2) precipitation of the H_2SO_4 with $BaCl_2$; (3) precipitation of the excess of barium and other earthy bases with Na_2CO_3; (4) evaporation of the filtrate with $PtCl_4$.

In the estimation, 10 grammes of the sample are ignited in a platinum basin with concentrated H_2SO_4, finishing with a blast. The residue is powdered in a mortar with a little hot water, washed into a 500 c.c. flask, and boiled for half an hour with 250 c.c. of water. A 10 per cent. solution of $BaCl_2$ is then introduced, 5 c.c. at a time, until no more precipitate forms. One drop of phenol-pthalein solution is then added, and sodium carbonate until a faint pink tinge is observed. The liquid is boiled, cooled, made up to the mark, and filtered. To 50 c.c. of the filtrate (= 1 gramme of the sample) HCl is added to slight acid reaction, then $PtCl_4$, and the liquid evaporated to dryness on the water-bath. The precipitate is washed with alcohol (specific gravity 0·848), dried at 100°, and weighed. For potassium salts ignition with H_2SO_4 is omitted.

The author lays stress on the following points: (1) Cautious addition of the H_2SO_4; (2) fine pulverization of the ignited mass in order to prevent calcium sulphate mechanically enclosing potassium sulphate; (3) avoidance of an excess of Na_2CO_3, which might cause decomposition of the precipitated $BaSO_4$.

From the table of results given, this method, which, in common with other methods, does not account for the entire potash present in samples of known composition, appears to be superior to the Lindo-Gladding process. C. A. M.

The Addition of Calcium Chloride to the Solution of a Fertilizer in the Determination of Potash. Rudolf de Roode. (*Jour. Amer. Chem. Soc.*, 1895, xvii., No. 1, p. 46.)—In order to allow platinum basins to be used in the Lindo-Gladding method, Huston recommended the addition of sufficient $CaCl_2$ to form calcium phosphate with the phosphoric acid present. The author finds that, in order to make this effective, it is necessary to filter off the precipitate formed by the $CaCl_2$ and NH_3, and then to add ammonium oxalate to the filtrate. As this involves two filtrations, the suggestion does not seem to be an improvement on the present alternative method. C. A. M.

Viscometrical Examination of Butter. C. Killing. (*Zeit. für angewandte Chemie*, 1894, pp. 643-645, and pp. 739, 740.)—The apparatus used by the author

consists of a wide glass cylinder, closed at the bottom by an indiarubber cork, through which passes a short tube, having its top ground to receive a sort of pipette. This holds about 50 c.c., and has an arrangement in its body to allow of the introduction of a small thermometer. The upper tube of the pipette, which passes through the top cork of the cylinder, is closed by a tap, and the pipette has three marks—one below the body and two above, the latter being placed about 1 cm. apart. The cork closing the top of the cylinder is made to remove in two halves, and a second thermometer is passed through one of these. The whole apparatus is fixed in a clamp, and a beaker is placed below to receive the fat.

The standard of viscosity is the time a definite volume of water at 20° C. takes to run out. The viscosity of butter is taken at 40° C., and it is essential that both thermometers should be compared with a standard thermometer, and a correction made if different.

In using the apparatus the top cork of the cylinder, with the thermometer, is removed and the pipette withdrawn. About 60 c.c. of the clear melted fat is cooled to 40·5°, the pipette thermometer inserted in its place, and the butter sucked to the upper of the two top marks. The tap is then closed, and the pipette placed in the cylinder; the latter is filled to the top with water at 42°, and the cork covers replaced. When both thermometers stand at 40°, the tap is slightly opened and the fat allowed to run slowly down to the lower of the upper marks. The tap is then opened wide, and the fat runs out into the beaker until it reaches the lowest mark, when the tap is closed and the time noted. The mean of two or three determinations, which should not vary more than $\frac{1}{4}$ to $\frac{1}{2}$ a second, is taken, and this compared with water as 100, gives the viscosity number.

In the author's apparatus, distilled water at 20° C. ran out in 80·33 seconds, and supposing a butter to take 3 minutes 42 seconds, this would give as the viscosity number

$$\frac{222{\cdot}00 \times 100}{80{\cdot}33} = 276{\cdot}3.$$

The following tables give the results obtained with different samples of margarines and butters:

A.—Margarines.

	Description.			Time running out. Min.	Time running out. Sec.	Viscosity Number.	Remarks.
1.	Dutch margarine			4	12·50	314·3	
2.	German margarine, M.D.	Quality	I.	4	13·66	315·8	From the same factory.
3.	,, ,,	,,	II.	4	11·66	313·3	
4.	,, ,, M.B.	,,	I.	4	11·66	313·3	All from factory. No. 4 contained earth-nut oil; Nos. 5 & 6 cotton-seed & sesame oil.
5.	,, ,,	,,	II.	4	13·83	315·9	
6.	,, ,,	,,	III.	4	11·83	313·5	
7.	Rotterdam margarine			4	12·16	313·9	
8.	German margarine, M.G.	,,	I.	4	12·38	314·2	From same factory.
9.	,, ,,	,,	II.	4	15·00	317·4	
10.	,, ,, M.H.	,,	I.	4	14·00	316·2	,,
11.	,, ,,	,,	II.	4	11·83	313·5	
	Mean ...	...		4	12·77	314·7	

B.—Butters.

Description.	Time running out.	Viscosity Number.
1. Westphalian	3 min. 42·00 sec.	... 276·3
2. Rhine	3 ,, 41·90 ,,	... 276·2
3. ,, ...	3 ,, 45·33 ,,	... 280·5
4. Dutch	3 ,, 42·16 ,,	... 276·5
5. Oldenburg	3 ,, 45·16 ,,	... 280·3
6. Westphalian	3 ,, 43·42 ,,	... 278·1
7. Holstein	3 ,, 46·00 ,,	... 281·3
8. Rhine	3 ,, 44·13 ,,	... 279·0
Mean ...	3 min. 43·76 sec.	278·5

Taking the mean numbers, the amount of margarine in an adulterated butter may be calculated from the formula :

$$x = (v - 278{\cdot}5)\frac{100}{314{\cdot}7 - 278{\cdot}5}, \text{ or } x = 2{\cdot}76(v - 278{\cdot}5), \text{ where } v = \text{viscosity number.}$$

The products used in the manufacture of margarine gave the following viscosity numbers :

German oleo-margarine	339·2
American ,, ...	332·7
Earth-nut oil	296·3
Sesame oil	273·9
Cotton-seed oil	258·9

A mixture of 75·6 parts of American oleo-margarine with 24·4 parts of cotton-seed oil gave the mean viscosity number of margarine 314·7. A mixture of 50 per cent. of each gave a viscosity number of 295·8, but the product was so fluid that it would have been unsaleable. It thus appears that it is impossible to make a butter from cotton-seed oil and oleo-margarine with the right viscosity number—viz., 278·5.

The one oil from which an artificial butter with a low viscosity number can be prepared is cocoa-nut oil, which gives 223·1, but according to the author this is no longer employed in the manufacture of margarine, since it has been found impossible to get rid of the taste.

Mixtures of butter and margarine with the respective viscosity numbers of 278·8 and 315·6 showed a proportionate increase in the numbers :

Butter Fat.		Margarine Fat.	Viscosity Number Found.	Corresponding to Margarine %.
95·17	+	4·83	280·20	3·81
75·53	+	24·47	287·56	23·83
55·70	+	44·30	295·50	45·42
42·45	+	57·55	300·16	58·09
25·20	+	74·80	306·09	74·23

The smallest amount of added margarine that can be detected will depend to a large extent on the amount of variation of butters among themselves, and this seems to be considerable. Butter from the milk of a cow fed on beetroot only gave a viscosity number of 270·76, whilst another cow fed exclusively on distillers' refuse produced a butter with viscosity number 278·23. Nevertheless, the author claims for this process superiority over the Reichert-Meissl method. C. A. M.

The Rapid and Accurate Analysis of Bone-black. W. D. Horne. (*Journ. Amer. Chem. Soc.*, 1895, xvii., 1, pp. 51-55.)—In new char the amount of moisture is of importance, being frequently limited by contract to 3 per cent. It is determined by heating 2 grammes for two hours in an air-bath at 140° C.

Calcium carbonate may be conveniently estimated in Lunge's nitrometer, using mercury. The flask containing the sample and the small tube of HCl is connected with the three-way cock of the nitrometer, and the liberated CO_2 measured with the usual corrections for temperature and pressure. The char in the flask is previously moistened with 3 c.c. of saturated solution of mercuric chloride, which absorbs any H_2S formed.

The carbon, iron, calcium sulphate, and insoluble ash are determined on one portion. This is prepared by first removing all particles of iron with a magnet, and then grinding to an almost impalpable powder. Two grammes of this are boiled in a beaker with 20 c.c. HCl for thirty minutes, and the beaker then filled up with boiling water. The residue settling down is washed several times by decantation, and then transferred to a weighed platinum Gooch's crucible with asbestos plug. It is then washed with 80 per cent. alcohol, followed by 90 per cent. alcohol, and finally with ether, after which it is dried in the oven at 100° and weighed. This gives the carbon and the ash, and the loss of weight on burning over a blast when deducted from this gives the carbon alone.

The acid filtrate is nearly neutralized with ammonia, and ammonium acetate added till the solution turns yellow, then a few drops in excess, and the liquid heated below 70° C. until the iron and aluminium phosphates are completely precipitated. The precipitates washed free from chlorides are dissolved in a 6-oz. flask by dilute H_2SO_4, 10 c.c. of sodium sulphite added and the liquid boiled until the iron is completely reduced and the SO_2 expelled, after which it is cooled and titrated with permanganate. If the aluminum is to be determined, the above precipitate may be treated with 150 c.c. of ammonium molybdate solution and filtered from the phosphoric acid. The iron and aluminum in the filtrate are then precipitated by ammonia, the precipitate filtered off, dissolved in HCl, and reprecipitated by ammonia, collected, ignited, and weighed. The two may then be separated by any of the known methods.

The filtrate from the iron and alumina precipitation which contains the $CaSO_4$ is acidified with HCl, the sulphuric acid precipitated by $BaCl_2$ and the $BaSO_4$ calculated to $CaSO_4$.

Calcium sulphide is estimated by evaporating 5 grammes of char nearly to dryness with 20 c.c. HNO_3, and after adding 20 c.c. of HCl again evaporating low to expel the HNO_3. The residue is taken up in HCl, and the sulphuric acid precipitated in an aliquot part of the filtered solution. From the $BaSO_4$ is deducted that found above as $CaSO_4$.

The physical conditions of the char should be thoroughly examined. The grist is estimated by shaking gently 100 grammes on sieves of known mesh and weighing what passes through.

The density is determined, both loose and packed, by introducing the char into a weighed 50 c.c. or 100 c.c. flask, making up to the mark, and weighing. From this the density and the weight per cubic foot is calculated.

The porosity is determined by introducing the char little by little into the weighed flask filled with distilled water. The flask is tapped to pack the char, and when filled up to the mark is heated on the water-bath to expel air. After cooling, the supernatant water is removed, and the flask and its contents weighed. The increase of weight over that of the flask packed with char gives the amount of contained water.

To determine the durability of a char under continued friction, the author has devised the following test: 25 grammes of the char are shaken ten times backwards and forwards in a sieve with circular holes one-fiftieth of an inch in diameter, and the dust which passes through weighed. Dust and char are then shaken together in a cylinder of turned iron two inches deep and four inches in diameter with six glazed porcelain marbles. After shaking 200 times the marbles are removed, the char sifted as before, and the increased weight of dust calculated to per cent. of the char used. Fairly constant results were obtained from different parts of the same sample. Thus a new char yielded 1·72, 1·46, and 1·76 per cent. of dust. Two grades made by one firm gave 2·16 and 2·16 per cent. in one case, and 2·86 and 2·87 per cent. in the other. Char which had been in use ten months gave 0·92 and 0·94 per cent., which showed that its wearing condition had improved by use, the softer parts having been separated.

C. A. M.

On the Examination of Linseed Oil and Boiled Linseed Oil. Dr. Hugo Amsel. (*Zeit. für angewand. Chemie*, 1895, Heft. iii., pp. 73-78.)—With the exception of the Köttstorfer number, none of the usual tests applied to an oil (*e.g.*, the specific gravity, iodine-number, elaidin reaction, etc.), is of much value in the case of linseed oil, since they give results varying so widely in different specimens of the pure oil.

The method proposed by Filsinger (*Chem. Zeit.*, 1894, 1005 and 1867), in which the sample is mixed with chloroform and alcohol, and examined with the polariscope, is useless when mineral oil, which is optically inactive, has been used to adulterate the linseed oil. Moreover, in the case of boiled oils the solution is often so dark as to prevent an accurate observation being made.

As the result of an experience of many years, the author declares that adulteration may be detected with certainty by determining:

1. The capacity of the oil to dry when smeared on glass.
2. The saponification number, and the behaviour of the alcoholic solution on adding water.

And, according to the results from the above,

3. The mineral matter.
4. The amount soluble in alcohol.

Pure linseed oil without "driers" ought to dry quite hard in three days at most when spread in a thin layer on glass. With the addition of 5 per cent. *driers* it should not require longer than twenty-four hours, which should also be the time taken by boiled linseed oil. The addition of only 5 per cent. of rape oil prevents the layer from becoming hard, even after eight days.

In testing an oil the Köttstorfer number is first taken, about two grammes being saponified in the usual way with alcoholic potash. Since mineral oils are not thus saponifiable, and the saponification number of rosin oils very low, the result will give

an approximate idea as to the character of the oil. The average saponification number (*i.e.*, the KHO required per 1000 of oil) of linseed oil is 188, while that for boiled linseed oil varies from 190 to 195.

The drying test is next made, and this will prove whether mineral oils be present. If present, the thin layer on the glass will not be hard after three days.

Another important characteristic of a pure linseed oil is that its alcoholic soap solution remains perfectly clear on adding water, whilst an oil adulterated with mineral oil, rosin, or resinated metallic oxides becomes milky. The following instances, selected from a long table, show this:

TABLE I.

	Saponification No.	Alcoholic Soap Solution + Water.	Calculated Addition from the Saponification No. per cent.
1. Linseed oil	188	Clear	
2. Boiled linseed oil	196	,,	
3. Blue rosin oil	13·5	Milky	
4. American mineral oil ...	2	,,	
7. Scotch mineral oil	9·6	,,	
10. Linseed oil + 5 per cent. mineral oil	177	,,	5·9
11. Linseed oil + 10 per cent. mineral oil	171·4	,,	9
16. Linseed oil + 20 per cent. rosin oil	156	,,	18
22. Boiled linseed oil + about 2·5 per cent. resinated metallic oxides	187	,,	About 3

The saponification number of No. 22 was so nearly normal that had the alcoholic soap solution remained clear it would readily have been passed as genuine.

TABLE II.—LINSEED OILS.

	Saponification No.	Alcoholic Soap Solution on addition of Water.	Iodine No.	Drying Capacity on Glass + 5 per cent Driers.
1.	183	Clear	180	Hard in 24 hours.
2.	188	,,	180	,, ,,
3.	173	Milky	—	Viscous after 24 hours.
4.	179	,,	112	After 5 days, as at beginning.
5.	189	Clear	180	Hard in 24 hours.
6.	180	,,	—	,, ,,
7.	174	Milky	—	Viscous after 24 hours.
8.	165	,,	157	Viscous after 48 hours.
9.	190	Clear	183·5	Hard in 24 hours.
10.	191	,,	167	After 5 days, as at beginning.
11.	190	,,	—	Hard in 24 hours.
12.	189	,,	—	Hard in 24 hours.

The foregoing tests showed that Nos. 1, 2, 5, 6, 9, 11, and 12 were pure linseed oils. Nos. 3 and 7 were adulterated with rosin oil; No. 8. with mineral oil; and Nos. 4 and 10 with rape oil.

TABLE III.—BOILED LINSEED OIL.

	Saponifica-No.	Alcoholic Soap Solution + Water.	Iodine No.	Drying Capacity.	Soluble in Alcohol, per cent.	Mineral Matter, per cent.
1.	117	Milky	—	After 3 days viscous		
2.	141	,,	153	Dry after 2 days.		
3.	188	,,	—	,, ,,		
4.	193	Clear	—	Hard in 24 hours.		
5.	138	Milky	128	Not quite hard after 2 days		
6.	153	,,	—	Dry after 2 days		
7	195	Clear	181	Hard in 24 hours		
8.	172	Milky	—	Dry after 2 days	26·3	
9.	199	Clear	174	Hard in 24 hours		
10.	92	Milky	148	Dry in 36 hours	50	
11.	198	Clear	183	Hard in 24 hours.		
12.	191	,,	—	,, ,,	24	
13.	197	,,	189	Hard in 24 hours.		
14.	189	Milky	165	Dry after 2 days.	32	
15.	193	Clear	169	Hard after 24 hours.	19·5	
16.	174	Milky	155	Still viscous after 3 days	19	0·21
17.	171·8	,,	146	,, ,, ,,	18	0·21
18.	175	,,	161	Dry after 2 days	25	0·23
19.	191	Clear	125	After 7 days as at first	8	
20.	125	Milky	—	Dry after 2 days	37·8	0·4
21.	190	Clear	—	Hard in 24 hours		
22.	193	,,	—	Hard in 18 hours		
23.	161·7	Milky	—	Viscous after 2 days		
24.	133	,,	—	Dry after 2 days		
25.	183	,,	—	,, ,,		

Of the above, Nos. 4, 7, 9, 11, 12, 13, 15, 21, and 22 were pure boiled linseed oil. No. 19 contained 50 to 60 per cent. of rape oil. Nos. 16 and 17 contained mineral oil. Nos. 1, 2, 3, 5, 6, 8, 10, 14, 18, 20, 23, 24, and 25 contained rosin, rosin oil, or resinated metallic oxides.

TABLE IV.—LINSEED OILS, THICKENED BY HEAT AND OXIDATION.

	Saponification No.	Alcoholic Soap Solution + Water.	Iodine No.	Per cent. Soluble in 98 per cent. Alcohol.
1.	195	Clear	94·4	18·5
2.	194	,,	104	17·7
3.	209	,,	—	9·2
4.	192	,,	—	6
5.	111	Turbid	—	49

Of these, No. 5 was adulterated with about 40 per cent. of rosin, while the others were pure linseed oils.

In the case of thickened oils, the determination of the amount soluble in alcohol is of value. About 1 gramme of the oil is mixed with 20 c.c. of alcohol, allowed to stand at the ordinary temperature for twenty-four hours, with constant shaking, and then filtered. For linseed oils the mean amount is about 25 per cent., while thickened oils always yield under 20 per cent. C. A. M.